STUDY OF V-CENTRES STABLE AT ROOM TEMPERATURE IN NaCl(Ca) CRYSTALS*

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Following X-irradiation of OH-free NaCl(Ca) crystals at room temperature, the authors observed new absorption bands at 360, 336 and 193 nm wavelengths, in addition to the V_2 band appearing in pure crystals at 223 nm. These new bands were assigned to V_F, V_1^M and V_2^M centres, respectively.

The M superscript refers to the presence of the divalent metal impurity, thus distinguishing the centres from similar centres in the pure crystal. In the case of X-irradiation at —80°C a new band was observed at 330 nm shown to be due to V_K^M centres. The models of the appearing centres are well-known, except in the case of V_1^M centres for which the authors propose a model.

I. Introduction

In previous papers we investigated the V-type centres created by X-irradiation in the KCl(Ca) system and their conversion [1, 2]. The results obtained in this system were comparatively simple and clear-cut since here only one V-type centre which can be considered stable appears at RT, i.e. the V_2^M centre created by the association of V_K^M centres. But in the case of NaCl(Ca), also according to our previous investigations, we are confronted with a more complicated situation. We had shown e.g. the appearance of V_F centres stable at RT [3], and the NaCl(Ca) system also exhibits a different behaviour concerning ionic conduction, since its conductivity, contrary to the KCl(Ca) system, is decreased by irradiation [4].

The paper gives further data concerning the V-type centres stable at RT appearing in the OH-free NaCl(Ca) system.

II. Experimental method

The crystals were grown free from OH by a method which we developed [5] from starting material purified in our laboratory [6]. 0.1 Mole% $CaCl_2$ was added to the melt; then to reduce the concentration of other impurities it was zone-refined several times. During zone-melting the Ca concentration

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* Dedicated to Prof. P. Gombás on his 60th birthday.

did not change considerably since the distribution coefficient of Ca in NaCl is approximately 1. At the final zone-melting a single crystal was grown at a speed of 3 mm/hour. In our experiments we have used the lower 2/3 part of the cylindrical crystal block of 200 mm length and 40 mm diameter. In the middle of the part used the Ca concentration, determined afterwards, was found to be 8×10^{-4} Mole/Mole.

In some of our experiments the OH-free crystals were submitted to subsequent annealing, consisting of keeping them in a furnace at 350°C in air for ~ 10 min, then cooling to RT in a few minutes.

We carried out experiments on crystals air-grown by the Kyropoulos method from reagent grade material some months earlier. In these cases the subsequently determined Ca concentration was 3×10^{-3} Mole/Mole.

The specimens for absorption measurements were cleaved to have a surface of 10×20 mm² and a thickness of 0.4—5.0 mm. The measurements were made with a UNICAM SP—700 spectrophotometer, placing a metal cryostat in one of its lightbeams when necessary. X-irradiation was carried out with a THX—250 deeptherapy apparatus at 200 kV, 20 mA using a 3.5 mm Al filter. In these conditions the dose rate was about 2500 R/min. The focussed light of a tungsten lamp was used (0.1 W/cm²) to illuminate the crystals.

III. Experimental results

III. 1. In Figs. 1 and 2 the absorption spectra of NaCl(Ca) crystals grown OH-free and X-irradiated at RT are shown for increasing doses. From the difference-curves the following facts can be established. In the beginning of colouration (irradiation time less than ~ 1 min, Fig. 1) a well-defined maximum in the UV region appears only at 336 nm growing nearly proportionally with the F band. With increasing dose the maximum at 336 nm approaches saturation and a new band with a maximum at 193 nm begins to develop (curves b and c of Fig. 2). The 193 nm band lies near to the limit of the measuring range of the SP—700. Therefore, its position was determined with a vacuum monochromator as well. In Fig. 3 it can be seen that the 193 nm band is superposed on the tail of the steeply rising β band.

III. 2. Curve a of Fig. 4 shows the absorption spectrum of a crystal X-irradiated at RT, exhibiting the 336 and 193 nm bands in the UV region. Curve b was obtained after warming the crystal to 80 °C. Under the effect of the few minutes warming the F' band disappears as expected and a slight decrease of the F band takes place. In the course of this process the 336 nm band becomes decomposed and the 193 nm band increases. Afterwards, the crystal was illuminated with white light and its absorption spectrum taken after illumination is shown by curve c. The changes in the F band can be
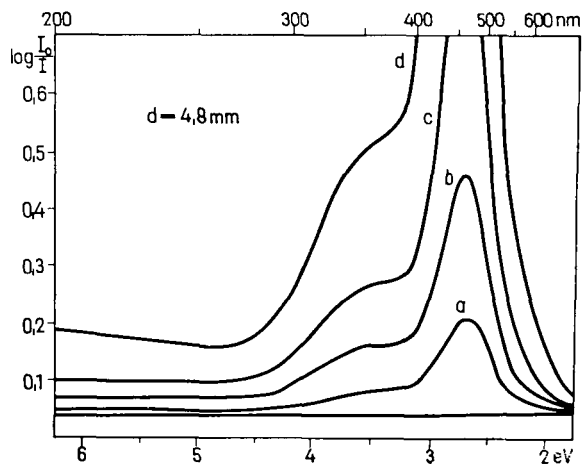
Fig. 1. Absorption spectra of OH-free NaCl(Ca). X-irradiation and measurement at RT. Irradiation times: a) 10 sec b) 30 sec c) 60 sec d) 150 sec
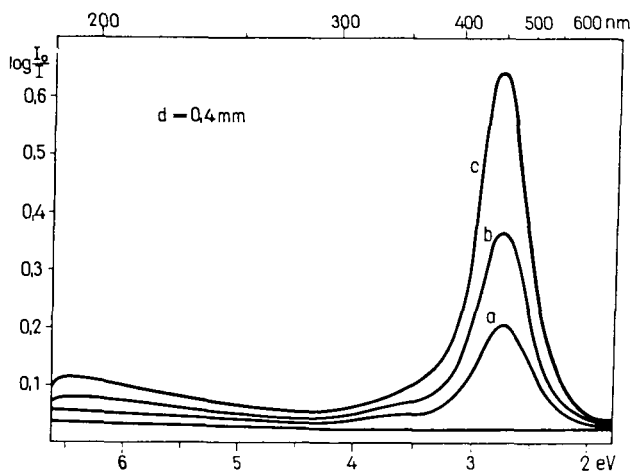

Fig. 2. Absorption spectra of OH-free NaCl(Ca). X-irradiation and measurement at RT· Irradiation times: a) 2 min b) 5 min c) 10 min

explained by bleaching and by $F \rightarrow Z_1$ conversion. Further, the illumination causes a decrease in the 193 nm band and an increase in the 336 nm band.

III. 3. Curve *a* of Fig. 5 was obtained on a crystal grown OH-free and X-irradiated at —80 °C (30 min). Beside the *F* band (and *F'*) a well-expressed maximum can be seen only at 333 nm. Warming to RT changes the spectrum. Curve *b* was obtained after warming for a few minutes and curve *c* after 40 minutes. A decrease takes place first in the *F* band maximum and mainly in the vicinity of 330 nm. The maximum of the remaining band lies at 336 nm,
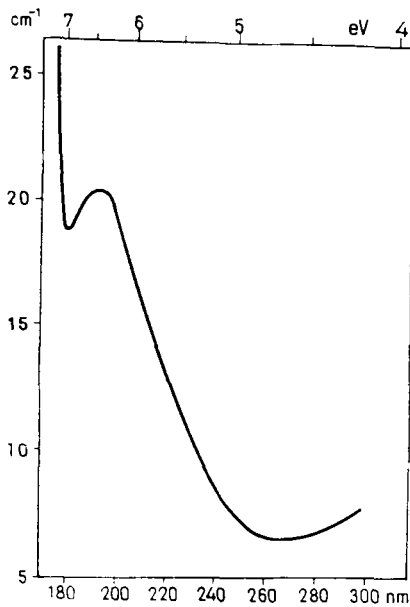
Fig. 3. Absorption spectrum of OH-free NaCl(Ca) in the vacuum UV region. X-irradiation (30 min) at RT, measurement at LNT
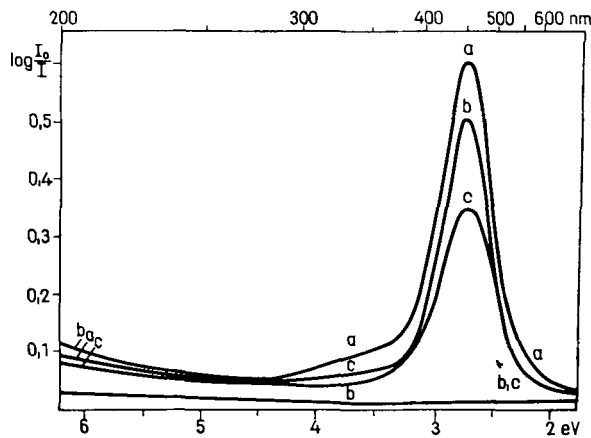

Fig. 4. Absorption spectra of OH-free NaCl(Ca). X-irradiation and measurement at RT. a) immediately after 2 min X-irradiation; b) after a short warming to 80 °C, c) after subsequent illumination with white light

that is, at the wavelength where a maximum also appears in crystals X-irradiated at RT. Keeping the crystal at RT for 40 minutes causes the F' band to disappear and the 336 nm band to decrease. This phenomenon is similar to the previous one observed in crystals X-irradiated at RT and warmed
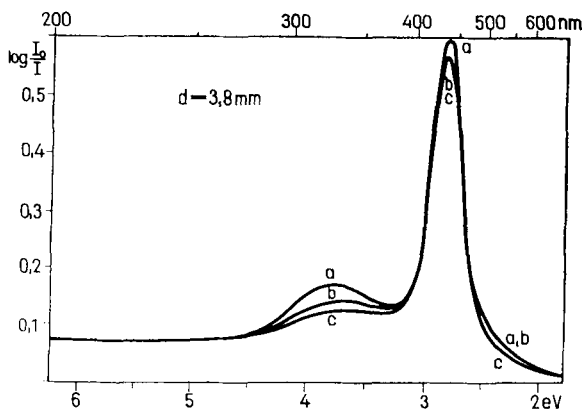
Fig. 5. Absorption spectra of OH-free NaCl(Ca). X-irradiation at $-80\,°C$ (30 min.), measurement at LNT, a) immediately after X-irradiation, b) after a short warming to RT, c) after 40 min at RT

to $80\,°C$. The only difference is that the process takes place faster at $80\,°C$ and after the disappearance of the F' band the conversion of the 336 nm band into the 193 nm band can also be plainly observed.

III. 4. In Fig. 6 the absorption spectrum of a crystal can be seen which was grown OH-free, then annealed and X-irradiated at RT. Evaluation of the curves corresponding to increasing doses reveals that in less colored crystals bands appear at 223 nm and 360 nm and the 193 nm band mentioned above grows considerably only at higher doses. Whether the crystal is kept for a few minutes in air or in an inert atmosphere during annealing does not affect the result. If an annealed crystal is X-irradiated after several days of recovery its behaviour becomes similar to that of an unannealed crystal.

III. 5. Fig. 7 shows the absorption spectra of a NaCl(Ca) crystal grown in the traditional way and X-irradiated at RT for different irradiation doses. First, at a broad maximum, appears 350 nm, then the 193 nm band becomes more and more pronounced. An analysis of the curves shows that the maximum at 350 nm consists of the previously observed 336 nm and 360 bands. According to our result, obtained here too, the 336 nm band decreases at RT mainly together with the F' band, and after the disappearance of the latter the decrease becomes slower.

III. 6. The peak positions and estimated half-widths of the 5 observed bands in the UV region are summarized in Table I. We should like to point out that the exact determination of peak positions in the 300—400 nm range is impossible because of the overlapping of the F band, the comparatively small extinction constants and the great half-widths. The exact data of the 193 nm band, superposed on the tail of the β band similarly cannot be determined. The data are given for LNT but they are not significantly different
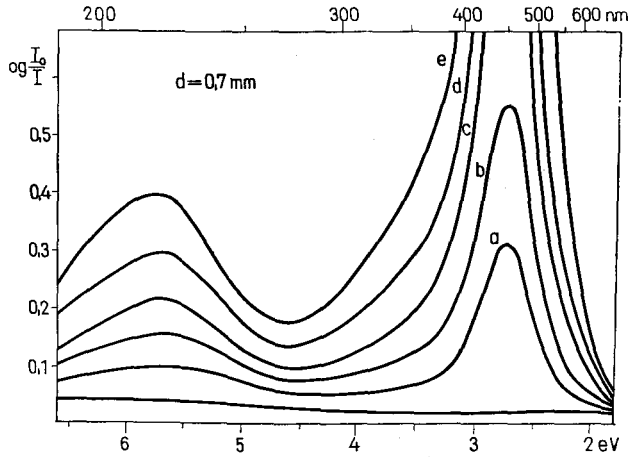
Fig. 6. Absorption spectra of OH-free grown and annealed NaCl(Ca). X-irradiation and measurement at RT. Irradiation times: a) 3 min b) 6 min c) 10 min d) 15 min e) 25 min
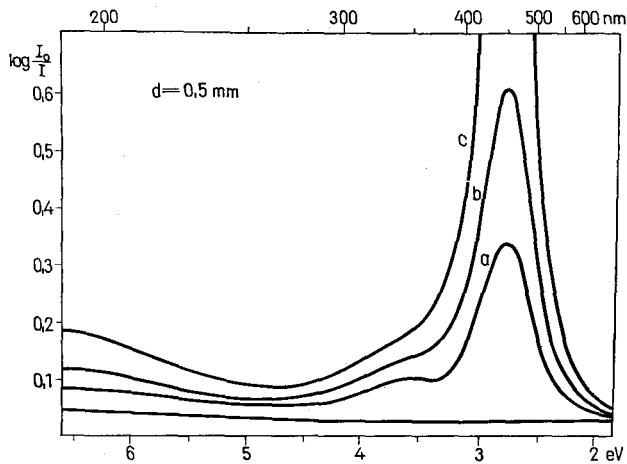

Fig. 7. Absorption spectra of an NaCl(Ca) crystal air-grown by the Kyropoulos method. X irradiation and measurement at RT. Irradiation times: a) 3 min b) 6 min c) 15 min

from RT data which can be explained by the mentioned inaccuracy and by the fact that they change only slightly with temperature.

III. 7. By examining and comparing the absorption and ESR spectra the 330 nm band can be assigned to the V_K^M centres proposed by HAYES and NICHOLS [7] and the 360 nm band to the V_F centres proposed by KÄNZIG [8]. ESR signals were not observed in connection with the other bands.

III. 8. The bands exhibit a measurable decrease at RT due to bleaching or to the conversion of the corresponding centres. From the initial part of the decrease which can be considered to be exponential we obtained data on the

Table I

Band maximum (nm)	Half-width (eV)	Life-time
193	1	> 1200 h
223	1	∼ 5 h
330	0.7	< 0.5 min
336	0.7	∼ 45 min
360	0.7	∼ 22 h

mean life-time of the bands at RT (Table 1). The value given for the 336 nm band refers to the process related to the disappearance of the F' band. After the disappearance of the F' band the life-time reaches 300 hours. The values obtained for the 330 and 360 nm bands agree with those obtained from ESR spectra, that is, in our crystals the mean life-time of V_K^M centres is certainly less than 0.5 min and that of V_F centres is about 22 hours.

IV. Discussion

IV. 1. We attribute all UV bands to V-type centres. In connection with this we should like to show that neither of the bands found between 300 and 400 nm is identical with the Z_3 band due to interstitial Ca^+ ions found by K. KOJIMA in additively coloured NaCl(Ca) crystals [9]. Our arguments are the following:

a) The maximum of the Z_3 band lies at 402 nm at LNT and we did not observe such a maximum.

b) Were the Z_3 band present, the Z_2 band should appear, too. Its maximum is at 474 nm on LNT and it widens the F band on the long wavelength side. We did not observe this either; that is, we found only the F' band on the long wavelength side of the F band.

c) We have shown that the 360 nm band, nearest to the Z_3 band is due to V_F centres and the 330 nm band may be attributed to V_K^M centres. As was mentioned in III. 1 the 336 nm band grows together with the F band in the initial stage of colouration, and since in this stage no other band is observable, it can be considered to be the V-type "partner" of the F band.

d) It is worth mentioning that we did not observe Z_3 and Z_2 bands even in the KCl(Ca) system [1], where the V bands do not overlap the Z_3 band.

IV. 2. In the following we deal with the models for the centres corresponding to the observed bands. To start with, the following can be stated:

a) In the case of the applied irradiation doses the observed bands are due to centres created mainly by the conversion of defects already existing in

the uncoloured crystal (so-called first stage of colouration). Atoms or ions in interstitial positions are not present for any considerable period.

b) Owing to the presence of Ca^{++} ions in the OH-free unannealed crystals the cation vacancy concentration is much higher than the anion vacancy concentration. Some of the Ca^{++} ions and the accompanying cation vacancies are associated to each other, and the other part is in a dissociated state, and in the process of colour centre formation it is mainly the latter which take part [10]. Most anion vacancies are present at RT in vacancy pairs. The OH-free grown and annealed crystal differs from the unannealed one in having a greater number of isolated vacancies. The increase in the number of isolated vacancies is indicated by the higher ionic conductivity of annealed crystals, exceeding the conductivity of unannealed crystals by about one order of magnitude. In crystals grown in the traditional way one part of the calcium forms molecular bonds [11, 12, 13] and in the colouration it is mainly the vacancy pairs which play an active part.

c) We did not observe V bands varying simultaneously proportionally with each other. Therefore, we assume the detected five bands to be due to five different centres.

d) The centres giving rise to the observed bands contain only one or two holes trapped by two or three halide ions.

e) Based on the results of H. N. HERSCH obtained on solutions [14] we assume that bands appearing in the 300—400 nm region are due to two-chlorine molecules or molecule-ions, and bands in the vicinity of 200 nm to three-chlorine ones.

IV. 3. The V_K^M centre giving rise to the 330 nm band and the V_F centre responsible for the 360 nm one satisfy the above conditions. The V_K^M centre is a $\langle 100 \rangle$ oriented Cl_2^- molecule ion situated in a vacancy pair. Its "partner" is an F centre. On the formation of a V_K^M centre and an F centre the number of cation vacancies in the crystal decreases by one. The V_F centre is also a Cl_2^- molecule ion but situated in two anion and one cation vacancy nearly $\langle 110 \rangle$ oriented. Its "partner" is an F centre. On the formation of a V_F centre and an F centre the numbers of cation and anion vacancies both decrease by one.

The centre giving rise to the 336 nm band is diamagnetic and we assume it to contain a Cl_2 molecule. Such a centre may be formed from the V_K^M centre by capturing a second hole. In the following we denote it by V_1^M, where the "1" subscript refers to the relationship with the V_1 centres observed in some pure crystals, which are stable only at quite low temperatures. In our opinion the Cl_2 molecule of the V_1^M centre is situated in a vacancy pair $\langle 100 \rangle$ oriented and locally neutral; it is more stable than the V_K^M centre. Its "partners" are either one F' centre or two F centres. On the formation of a V_1^M centre and an F' centre, only the number of cation vacancies decreases by one, and on the

formation of a V_1^M centre and two F centres the number of anion vacancies decreases, too.

Based on the above results and deductions, the processes shown in Fig. 5 can be explained in the following way. When the crystal is kept at RT for a few minutes (curve b) the unstable V_K^M centres are destroyed by recombination with F centres. As a result of further warming (curve c) the F' centres are totally annihilated through recombination with V_1^M centres.

Let us note that the creation of V_F and V_1^M centres accompanied by the "partner" F centres equally reduces the number of anion and cation vacancies. Compare now the formation of V_F and V_1^M centres in OH-free grown annealed crystals and in crystals air-grown by the Kyropoulos method. Though the anion and cation vacancy concentrations are high in both types of crystals, yet in the initial stage of colouration V_F centres are created in the former type and V_1^M centres in the latter. In our opinion the difference is related to the fact that in OH-free, annealed crystals immediately after annealing mainly isolated vacancies are present while in a crystal grown in the traditional way the vacancies are associated ones. In the first case conditions are favourable for the formation of V_F centres, and in the second for the formation of V_1^M centres. In OH-free unannealed crystals, too, there are associated vacancies present, therefore V_1^M centres are also created here at the beginning of colouration. But since the number of associated pairs is comparatively small, the concentration of V_1^M centres quickly approaches a saturation value. V_F centres appear in an observable number only at high doses, when we already reach the second stage of colouration.

Accepting the above facts, the concentration of vacancy pairs (anion vacancies) in the uncoloured crystals can be estimated in the given case from Fig. 1. Namely, this is the concentration at the moment when the V_1^M centres are near their saturation value (curve c) and no other V-type centres are yet present in a detectable quantity. Calculation gives the concentration of anion vacancies in the given uncoloured crystal to be approximately 9×10^{15} cm^{-3}, i.e. 8×10^{-7} Mole/Mole. This value is high compared with the RT equilibrium concentration. It is possible that the concentration is increased by frozen-in anion vacancies, but neither do we exclude the possibility that anion vacancies are brought into the crystal by some trace impurity. In the case of NaCl even the purity of the starting material is about 8×10^{-7} Mole/Mole.

The centres giving rise to the 193 nm and 223 nm bands are diamagnetic and in our opinion they contain Cl_3^- molecule ions. The first we denote by V_2^M, because we think that they are created similarly to V_2^M centres in the KCl(Ca) system from V_K^M centres [1]. In the V_2^M centres the Cl_3^- ion is situated in 2 cation and 1 anion vacancy in the vicinity of 2 Ca^{++} ions. But we leave open the question, open in the literature, too [7, 10, 15, 16, 17], whether the Ca^{++} is closely bound to the V_K^M and consequently to the V_2^M centres or not. We con-

sider the centres giving rise to the 223 nm band to be similar to the V_2 centres responsible for the 223 nm band observed in pure NaCl crystals. Since V_2 centres in the pure crystal appear at the beginning of colouration, it seems probable to us that they are created from vacancies already existing in the crystal. Therefore we consider the V_2 centre to consist of a Cl_3^- molecule ion situated in a 2 anion and 1 cation vacancy. This model agrees with that suggested previously for V_3 centres [18]. In our opinion the V_3 centre is more probably related to interstitially placed halogen, which assumption is supported by hardening studies [15]. Both the V_2^M and V_2 centres may be $\langle 100 \rangle$ oriented but we think that other orientations are also possible.

The model constructed for the V_2^M centre is supported by the experiment mentioned in III. 2 concerning the fact that the V_2^M centres may be formed from V_1^M centres by thermal activation, and under the effect of white light may be transformed back into V_1^M centres. Therefore, in our opinion the following transformations may possibly take place:

$$V_1^M + F \rightarrow V_K^M + \boxminus ,$$
$$2\,V_K^M \rightarrow V_2^M$$

and
$$V_2^M \cdot \cdot \ \boxminus \rightarrow V_1^M + \boxplus .$$
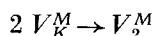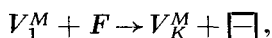
In conclusion we summarize the observed V centres in Table II, indicating the positions of band maxima measured at LNT, the possible models and the probable orientation of the centres. A question-mark denotes models requiring further support. For this purpose luminescence and ionic conductivity measurements are under way and the first informative measurements indicate that the decrease of ionic conductivity is caused by V_2^M centres.

Table II

Centre	Abs. max. nm	Orientation	Possible model
V_K^M	330	100	Cl_2^- in vacancy pair ($+$ Ca^{++} ?)
V_F	360	110	Cl_2^- in 2 anion vacancy $+$ 1 cation vacancy
V_1^M	336	100?	Cl_2 in vacancy pair?
V_2^M	193	100?	Cl_3^- in 1 anion and 2 cation vacancy ($+$ 2 Ca^{++})?
V_2	223	100?	Cl_3^- in 2 anion and 1 cation vacancy?

Acknowledgment

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ИССЛЕДОВАНИЕ *V*-ЦЕНТРОВ, СТАБИЛЬНЫХ ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ, В КРИСТАЛЛАХ NaCl(Ca)

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Резюме

Авторы наблюдали в NaCl(Ca) кристаллах, несодержащих OH, под действием рентгеновского облучения кроме V_2 полосы, находящейся в чистых кристаллах тоже на 223 нм, новые полосы поглощения на длинах волн 360, 336 и 193 нм, причисленные ими к $V_F{}' = V_1^M$ и V_2^M-центрам. (Буква «М» обозначает наличие двухвалентной металлической примеси, чтобы различать их от соответствующих центров чистого кристалла.) В случае облучения при температуре —80° С наблюдалась новая полоса на 330 нм и было показано, что эта полоса происходит из V_K^M-центров Модели перечисленных центров известны исключая V_1^M центров, для которых авторы предлагают модель.